Site-Specific Hydrogen Reactivity and Reverse Charge Transfer on Ge(111)-$c(2\times8)$

Tom Klitsner and J. S. Nelson
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 29 July 1991)

Scanning tunneling microscopy (STM) and first-principles pseudopotential calculations are used to show that the equilibrium binding site for hydrogen on Ge(111)-$c(2\times8)$ is the rest-atom site. Our calculations show the hydrogen-rest-atom configuration is 0.7 eV lower in energy than the hydrogen-adatom configuration. Reaction at the rest-atom site causes very local rest-atom to adatom reverse charge transfer, and this site-specific chemistry is imaged directly using STM measurements in combination with these calculations.

PACS numbers: 61.16.Di, 68.35.Bs, 73.20.At, 82.65.My

The interaction of hydrogen with semiconductors is of great interest for both technological and fundamental reasons. Hydrogen can passivate the electrical activity of dangling bonds both in the bulk and on the surface of materials, and this has many important consequences [1]. For instance, hydrogen can deactivate shallow impurity states as well as passivate deep defect and impurity states. Hydrogen can also unreconstruct surfaces, and hydrides play an important role as intermediates in chemical vapor deposition processes, such as those using silanes and germanes to produce epitaxially grown Si and Ge layers, and Si/Ge alloys and heterostructures. In fact, while much of the past work has focused on Si, interest in Ge has been increasing due largely to the unique electronic properties of these Si/Ge overlayer structures [2].

The reaction of hydrogen with Si(111) and Ge(111) surfaces has been the subject of extensive experimental and theoretical studies. Recent scanning-tunneling-microscopy (STM) work has shown there exists at least two reaction stages for hydrogen on Si(111)-7×7 [3,4]. Although previous work [5] has shown site specificity for the dissociative reaction of NH_3 on Si(111)-7×7, no such site specificity has been observed for hydrogen. In this Letter, we show, both experimentally and theoretically, that it is energetically favorable for a hydrogen atom to react at a particular dangling-bond site (the rest-atom site), inducing very localized rest-atom to adatom charge transfer.

The STM system used for these studies is a home-built four-quadrant tube design, mounted on a piezoelectric walker for coarse approach. The STM is housed in an ultrahigh-vacuum chamber with a measured base pressure of 4×10^{-11} torr. The Ge(111) sample was cleaned *in situ* by ion sputtering (2 keV Xe^+) while holding the sample at 500 °C and then post-annealing to 800 °C. This procedure results in a clean, multidomain Ge(111)-$c(2\times8)$ surface as determined from Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and STM images. The surface was then exposed to a 1-keV H^+ beam (1×10^{-6} A/cm^2) at 500 °C after which it was quenched to room temperature. After exposure to the hydrogen beam, the surface retained its bright, low-background $c(2\times8)$ LEED pattern, and no contamination was observed in the AES spectrum. The STM images reveal the same $c(2\times8)$ structure as previously, with what we interpret as a very low ($\lesssim 0.01$ monolayer) but fairly uniform coverage of hydrogen-reacted rest-atom sites. A larger reacted fraction of the surface can be obtained by exposure at lower temperatures; however, this also results in much more adatom disorder, making interpretation of the results quite difficult.

In this experiment, we expose the surface to a H^+ ion beam rather than an atomic hydrogen source. It has been shown [6] that during H^+ bombardment, implanted hydrogen reacts at bulk defect sites and is trapped. At elevated temperatures, the trapped hydrogen will then diffuse back to the surface as atomic hydrogen where it can be desorbed. Effectively, we then have an atomic hydrogen source within our sample. When the sample is subsequently quenched, we can then obtain a snapshot of the sites that have reacted at high temperature just prior to quenching. Previous work [7] has shown that only the monohydride is formed at the temperatures used in this study ($T > 400$ K).

We also perform first-principles self-consistent pseudopotential calculations [8] to compare with the STM results. In this calculation, the wave functions were expanded in plane waves with kinetic energy up to 10 Ry (3600 plane waves for the 29-atom unit cell), and the charge density was sampled at three k points in a 2×2 irreducible Brillouin zone. The slab used for this calculation has eight atomic layers, with the top layer consisting of a hexagonal 2×2 unit cell containing one adatom and one rest atom (see the discussion below), and the bottom layer consisting of a hydrogen-terminated 1×1 surface. The bottom two layers are held fixed, while the top six are allowed to relax.

Figure 1 shows a model of the $c(2\times8)$ structure. The adatoms which make up the $c(2\times8)$ structure are very similar to the adatoms in the Si(111)-7×7 structure. However, in contrast to the 7×7 structure, which has twice as many adatoms as rest atoms (first-layer atoms not bonded to adatoms), the $c(2\times8)$ structure has a 1:1 ratio of adatoms and rest atoms. Northrup has previously pointed out that there should be charge transfer from the adatom to the rest-atom dangling bonds [9]. On $c(2\times8)$, because of the equal number of adatom and rest-atom sites there should be fairly complete charge transfer, leaving the adatom dangling-bond state nearly completely empty, and the rest-atom dangling bond near-

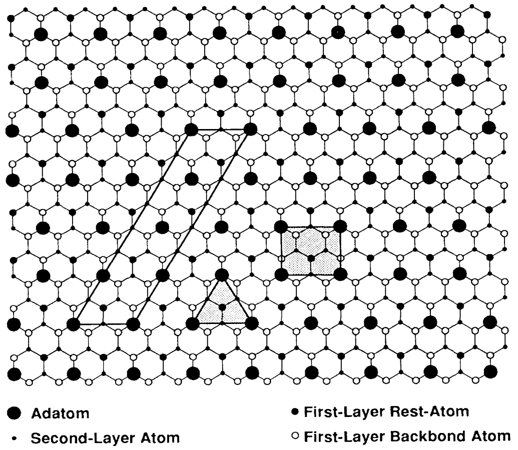


FIG. 1. Model of Ge(111)-$c(2\times8)$. The reconstruction is built from adatoms residing on the T_4 sites of the bulk-terminated 1×1 surface. Both the adatoms and the rest atoms (first-layer atoms not bonded to adatoms) have unterminated dangling bonds. Note that there are two symmetries for the rest atoms (see shaded regions): one symmetrically surrounded by three adatoms, and one asymmetrically surrounded by four adatoms.

ly completely filled.

The general features seen in STM images of Ge(111)-$c(2\times8)$ have been described previously [10]. More recent observations describe some of the more detailed features [11]. Figure 2 shows a dual-polarity STM image of Ge(111)-$c(2\times8)$ after hydrogen reaction. An occupied-state and an unoccupied-state image are obtained simultaneously, as in Ref. [10], by tunneling at one bias polarity during the forward part of each scan in the raster and reversing the polarity on the return part of each scan. The two images can then be superimposed to show the relative conformation of filled and empty electronic states. The unoccupied-state image in Fig. 2 has a straightforward interpretation. Our calculations show the primary unoccupied surface states are all strongly localized on the adatom site (the state shown has the largest calculated unoccupied-surface-state density, Fig. 3), indicating, as expected, that the unoccupied-state tunneling images correspond to the adatom site [12]. In the undisturbed part (lower right quadrant) of the occupied-state image, there are apparent protrusions at both rest-atom and adatom positions (though this is somewhat tip and bias voltage dependent [11]). Our calculations show the primary occupied surface state (this state has about 5 times the surface charge density of any other calculated band) is predominantly localized on the rest-atom site (Fig. 3); however, for the occupied-state case we find there exist other bands between this state and the Fermi energy which have significant surface charge density around the adatom site, and the adatom is physically higher than the rest atom. Therefore, one expects protrusions in the tunneling image at both the adatom and rest-atom sites, in good agreement with our occupied-state images. When the occupied- and unoccupied-state STM images are superimposed (Fig. 2), it is easy to identify both the adatom sites (in whitish blue) and the rest-atom sites (in orange). This is in contrast to STM images of Si(111)-7×7 which are dominated by the adatom dangling bonds at both bias polarities.

Figure 2 also contains a reacted area of the surface. Certain adatom sites show up as brighter spots in the

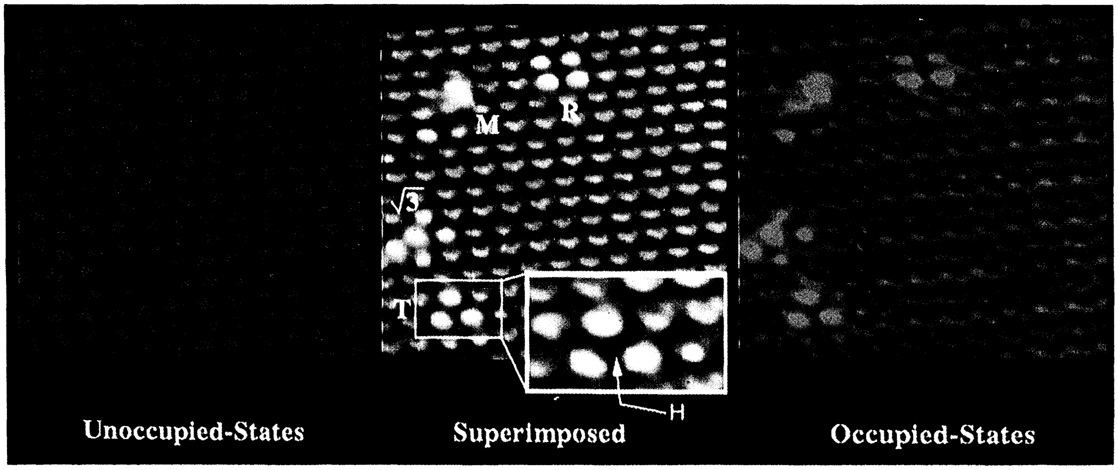
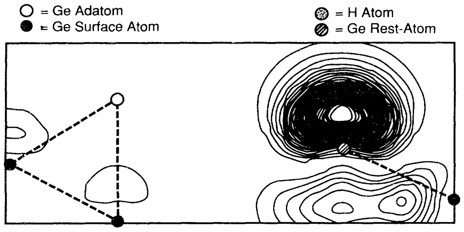
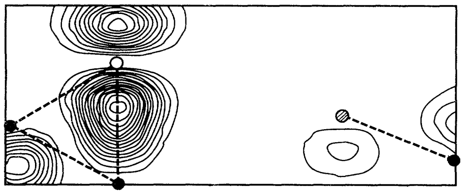


FIG. 2. Dual-polarity STM images of hydrogen-reacted Ge(111)-$c(2\times8)$ ($V_{\text{bias}}=\pm1.5$ V, $I=1$ nA). Unoccupied-state image: Protrusions correspond to adatoms. Note the adatoms around the reacted sites are nearly indistinguishable from the other adatoms. Superposition of occupied- and unoccupied-state images: In the unreacted region the bluish protrusions correspond to adatoms and the orange to rest atoms. Hydrogen reacting at the two different rest-atom geometries transfers charge back to the surrounding adatoms forming the bright triangle (T) and the asymmetric rectangle (R). Inset: Close-up of a bright triangle. Note the hydrogen-reacted rest-atom site has become dark due to the saturation of that dangling bond. Occupied-state image: In the unreacted region, both adatom and rest-atom sites are visible forming the observed hexagonal pattern. The origin of the bright triangle and rectangle is a large increase in occupied-state density at particular adatom sites.

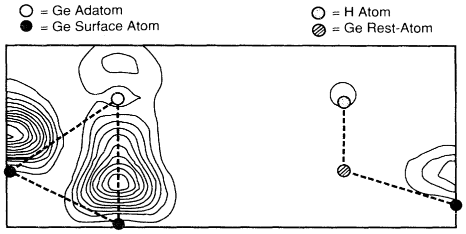


Occupied State Charge Density

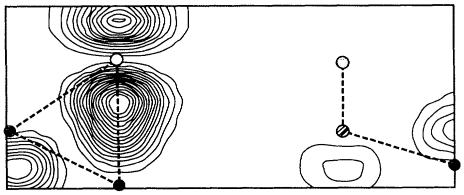


Unoccupied State Charge Density

FIG. 3. First-principles calculations of Ge(111)-2×2. Unoccupied-surface-state contours: Note the unoccupied-state density is strongly localized on the adatom site. Occupied-surface-state contours: The charge density is localized on the rest-atom site. Other occupied states exist which contribute surface charge density to the adatom as well; however, it is the state shown here which is primarily involved in subsequent charge transfer.



Occupied State Charge Density



Unoccupied State Charge Density

FIG. 4. First-principles calculation of hydrogen-reacted Ge(111)-2×2. Unoccupied-surface-state contours: Note that the unoccupied-state density is nearly unchanged after hydrogen reaction at the rest-atom site. Occupied-surface-state contours: Hydrogen forms a very strong, almost ionic, bond with the rest-atom site, passivating the rest-atom dangling bond. The adatom site shows a large increase in charge density due to reverse charge transfer from the hydrogen-reacted rest-atom site.

occupied-state and superimposed images. The two features on which we will focus are the symmetric triangle (*T*) and the asymmetric rectangle (*R*) of bright adatoms. These two features decorate the surface with a roughly uniform coverage of $\lesssim 0.01$ monolayer after H^+ exposure. We will show that these features are caused by a reverse charge-transfer process, and it is these two features we associate with hydrogen reaction. Also shown in Fig. 2 are examples of features that also appear bright in the dual-polarity images, but are not associated with hydrogen reaction at the surface. The feature labeled $\sqrt{3}$ has been described previously [10] and is associated with a local $\sqrt{3}\times\sqrt{3}$ configuration of adatoms. It appears bright because there is no central rest atom in this configuration to which the adatoms can transfer charge. The bright feature labeled *M* appears to be associated with a missing adatom, and is an example of a feature that appears bright at both tunneling polarities. This indicates the feature is probably actually physically higher than the equilibrium adatoms. Such features are relatively rare, and do not appear more frequently on the reacted or unreacted surface.

As we indicated, the origin of the bright triangles (*T*) and rectangles (*R*) of adatoms can be explained by a simple reverse charge-transfer process. Hydrogen reacting at a rest-atom site forms a strong covalent bond. The excess charge density that was residing on the unreacted rest-atom site must then be transferred back to the nearest unoccupied states, i.e., the surrounding adatom sites. This is similar to the process inferred from spectroscopic techniques for the reaction of NH_3 and SiH_4 on Si(111)-7×7 [5,13]. In the $c(2\times8)$ reconstruction there are two symmetries for rest-atom sites (see Fig. 1). The rest-atom sites in the hexagonal 2×2 units are surrounded symmetrically by three adatoms. Hydrogen reaction at these sites will transfer charge symmetrically back to those three surrounding adatoms which leads to the bright symmetric triangle features (*T*). The rest-atom sites in the rectangular units with $c(4\times2)$-like symmetry are surrounded by four adatoms but reside closer to two of the adatoms. Hydrogen reaction at these sites transfers more charge to the two nearer sites than the two more distant adatom sites, which leads to the bright asymmetric rectangular feature (*R*). Our first-principles calculations also clearly show this charge transfer (Fig. 4). In particular, the calculations show a large increase (when compared with Fig. 3) in occupied-surface-state density at the adatom site after hydrogen reaction at the rest-atom site, but virtually no change in the unoccupied-surface-state density at the adatom site. This is in excellent agreement with the occupied- and unoccupied-state tunneling images. Note, in particular, that while the occupied-state (and superimposed) image shows the characteristic triangular or rectangular features, those sites in the unoccupied-state image are virtually indistinguishable from other adatom sites. It should be noted that this calculation corresponds to every rest atom on the surface reacting with a hydrogen atom instead of the reaction of one isolated rest atom. However, both our calculations and experimental observations indicate that the observed electronic effects are very localized. Therefore, while qualitatively the results would not change, these calculations do show about 3 times the transferred charge residing on the adatom than would occur for the isolated-rest-atom case.

Careful examination of these sites also reveals that the hydrogen-reacted rest-atom site has become dark in the dual-polarity images (see inset in Fig. 2). The hydrogen-germanium bond is very strong and effectively passivates the rest-atom dangling-bond state. There are then no surface states near the Fermi energy at these reacted sites, which results in the dark rest-atom site observed in the STM images. This is similar to the effect seen when hydrogen reacts at adatom dangling bonds on Si(111)-7×7. The absence of states near the Fermi energy at the hydrogen-reacted rest atom is also clearly shown in our calculated charge contours (Fig. 4).

After examining many tunneling images such as these, we find no evidence for significant hydrogen-adatom reaction, i.e., we find no lone adatom sites becoming darker as a result of the dangling bond being saturated as was seen for room-temperature hydrogen reaction on Si(111)-7×7. Our first-principles calculations also show that the rest-atom site is preferred over the adatom site by 0.7 eV for hydrogen reaction. This is in contrast with experiments which show hydrogen does not appear to react preferentially at adatom or rest-atom dangling bonds [3,4]. We believe this discrepancy can be explained by the difference in exposure techniques in this work compared with previous work. When a room-temperature surface is exposed to hydrogen atoms, the hydrogen immediately reacts with either the rest-atom or the adatom dangling bonds. The 0.7-eV difference in energy between the two sites is too small compared to the kinetic barrier to result in any site specificity at room temperature. With the technique used in this work, we are able to react a small portion of the surface at an elevated temperature, which allows the hydrogen to find its lowest-energy binding site.

We can also gain physical insight, from study of the calculated total valence charge-density contours and relaxed atomic positions (not shown), into why the hydrogen-reacted rest-atom site is lower in energy than the reacted adatom. When hydrogen reacts at the rest-atom site, saturation of the dangling bond reduces the Coulomb repulsion that, for the unreacted site [12], exists between the dangling-bond electron cloud and the rest-atom backbonds. This allows the rest atom to relax to a position very close to its bulk lattice spacing. The neighboring adatom site is affected very little. In particular, the delocalized T_4 bond complex, on which the stability of the T_4 adatom site depends, is left undisturbed. On the other hand, when hydrogen reacts at the adatom site, the neighboring rest-atom sites, which now have partially filled dangling bonds, cannot relax as far towards the surface due to the increased Coulomb repulsion. The adatom relaxation also changes dramatically. Hydrogen reaction at the adatom dangling bond pulls charge from the T_4 bond complex. This causes the adatom backbonds to become more localized, which in turn increases the bond-bending repulsion between the adatom backbonds and the underlying first-layer backbonds. This forces the adatom further from the surface, increasing the strain in the backbonds, and decreasing the amount of fourfold coordination found for the unreacted adatom. This high degree of backbond strain introduced by reaction at the adatom may also play a role in hydrogen etching of the adatoms that occurs with additional exposure to atomic hydrogen. We find then that hydrogen reaction at the adatom site leads to higher-energy configurations for both the adatom and the rest atom than does hydrogen reaction at the rest-atom site.

In summary, we have shown, using dual-polarity STM images and first-principles calculations, that hydrogen reaction at the rest-atom site on Ge(111)-$c(2\times8)$ is energetically preferred over the adatom site. The difference in energy between the two sites, as determined by our calculations, is 0.7 eV. This reaction induces very localized charge transfer from the rest atom to the surrounding adatom sites, which can be imaged directly with the STM, in excellent agreement with our first-principles calculations.

We wish to thank R. S. Becker and B. S. Swartzentruber for very important and helpful discussions. This work was supported by DOE Basic Energy Sciences, Office of Materials Science, Contract No. DE-AC04-76DP00789.

---

[1] S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A **43**, 153 (1987).

[2] T. P. Pearsall, Crit. Rev. Solid State Mater. Sci. **15**, 551 (1989).

[3] J. J. Boland, J. Phys. Chem. **95**, 1521 (1991); Surf. Sci. **244**, 1 (1991).

[4] K. Mortensen, D. M. Chen, P. J. Bedrossian, J. A. Golovchenko, and F. Besenbacher, Phys. Rev. B **43**, 1816 (1991).

[5] R. Wolkow and Ph. Avouris, Phys. Rev. Lett. **60**, 1049 (1988); Ph. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).

[6] S. T. Picraux, F. L. Vook, and H. J. Stein, Inst. Phys. Conf. Ser. **46**, 31 (1979); H. J. Stein, Bull. Am. Phys. Soc. **26**, 781 (1981).

[7] John E. Crowell and Guangquan Lu, J. Electron Spectrosc. Relat. Phenom. **54/55**, 1045 (1990).

[8] A. R. Williams and J. Soler, Bull. Am. Phys. Soc. **32**, 562 (1987); see also C. Woodward, B. I. Min, R. Benedek, and J. Garner, Phys. Rev. B **39**, 4853 (1989).

[9] John E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).

[10] R. S. Becker, B. S. Swartzentruber, J. S. Vickers, and T. Klitsner, Phys. Rev. B **39**, 1633 (1989); R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, Phys. Rev. Lett. **54**, 2678 (1985).

[11] E. S. Hirschorn, D. S. Lin, F. M. Leibsle, A. Samsavar, and T.-C. Chiang, Phys. Rev. B **44**, 1403 (1991).

[12] The calculations for the unreacted surface are similar to those performed in Robert D. Meade and David Vanderbilt, Phys. Rev. B **40**, 3905 (1989).

[13] Ph. Avouris and F. Bozso, J. Phys. Chem. **94**, 2243 (1990).

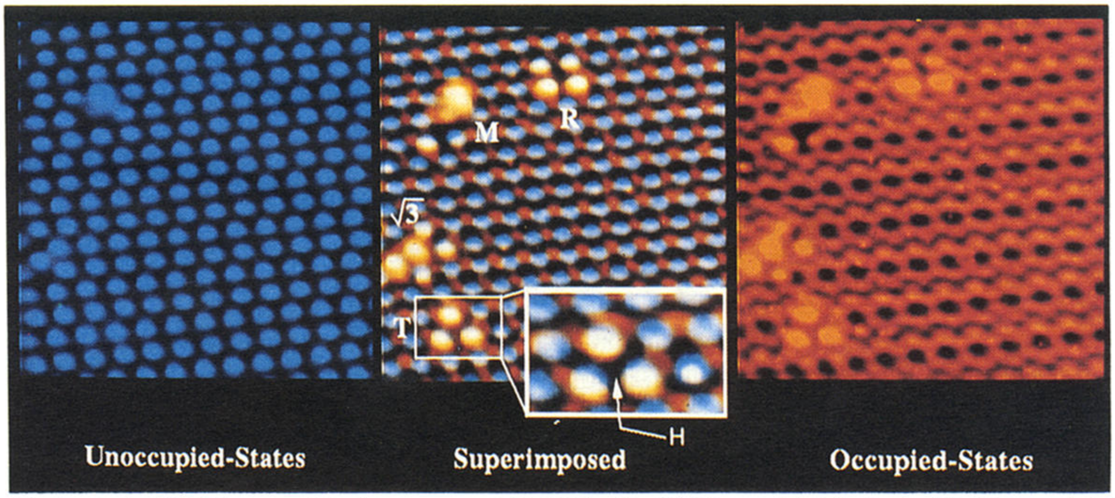


FIG. 2. Dual-polarity STM images of hydrogen-reacted Ge(111)-$c(2\times8)$ ($V_{\text{bias}} = \pm 1.5$ V, $I = 1$ nA). Unoccupied-state image: Protrusions correspond to adatoms. Note the adatoms around the reacted sites are nearly indistinguishable from the other adatoms. Superposition of occupied- and unoccupied-state images: In the unreacted region the bluish protrusions correspond to adatoms and the orange to rest atoms. Hydrogen reacting at the two different rest-atom geometries transfers charge back to the surrounding adatoms forming the bright triangle (T) and the asymmetric rectangle (R). Inset: Close-up of a bright triangle. Note the hydrogen-reacted rest-atom site has become dark due to the saturation of that dangling bond. Occupied-state image: In the unreacted region, both adatom and rest-atom sites are visible forming the observed hexagonal pattern. The origin of the bright triangle and rectangle is a large increase in occupied-state density at particular adatom sites.